

Self-assembly of triorganotin(IV) moieties with 2,3,4,5-tetrafluorobenzoic acid and 4,4'-bipy, triphenylphosphine oxide or phen: Syntheses, characterizations and supramolecular structures

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Received 29 July 2006; received in revised form 16 September 2006; accepted 21 September 2006

Available online 5 October 2006

Abstract

A series of triorganotin (IV) complexes with 2,3,4,5-tetrafluorobenzoic acid and mixed-ligands of the types: $R_3Sn(O_2CC_6HF_4)_m \cdot L$ ($m = 1$, $L = 0$, $R = Ph$ **1**; $m = 1$, $L = Ph_3PO$, $R = Ph$ **4**, Me **5**), $[R_3Sn(O_2CC_6HF_4)]_m \cdot L$ ($m = 2$, $L = 4,4'$ -bipy, $R = Ph$ **2**, Me **3**; $m = n$, $L = 0$, $R = Me$ **6**), and $[R_3Sn(O_2CC_6HF_4) \cdot (H_2O)]_m \cdot L \cdot C_2H_5OH$ ($m = 2$, $L = Phen$, $R = Ph$ **7**, Me **8**), (4,4'-bipy = 4,4'-bipyridyl; Phen = 1,10-phenanthroline), have been synthesized by the reaction of triorganotin chloride and 2,3,4,5-tetrafluorobenzoic acid in the presence of mixed-ligands: 4,4'-bipy, triphenylphosphine oxide, or phen. All complexes were characterized by elemental analysis, IR, 1H , ^{13}C , ^{119}Sn NMR spectroscopy analysis. Except for **5** and **8**, all the complexes were also characterized by X-ray crystallography.

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Keywords: 2,3,4,5-Tetrafluorobenzoic acid; Self-assembly; Supramolecular structures; Triorganotin

1. Introduction

Supramolecular chemistry has increasingly emerged as a powerful field for construction of molecular-based devices with advanced functions and well-defined structures [1]. A number of supramolecular architectures had been successfully designed and synthesized through metal-directed self-assembly of organic ligands and metal ions or molecular hydrogen bonds and π - π or C-H $\cdots\pi$ stacking interactions [2,3]. In recent years, organotin(IV) derivatives have received much attention, owing to the enormous variety of intriguing structural topologies and their unexpected

properties for potential practical applications [4]. A biologically interesting donor is the carboxyl group, which coexists with the nitrogen atom in several relevant species. In our previous work, we have reported on the chemical, structural, polymer properties of a series of similar organotin(IV) carboxylate complexes [5]. As an extension of this research, we are interested in utilizing the organic ligand with non-coordinated functional groups such as N and O atoms in conjunction with aromatic carboxylate groups is considered for the creation of supramolecular assemblies by non-covalent bonds (hydrogen bonds or π - π and C-H $\cdots\pi$ stacking interaction). To evaluate some of these features of coordination complexes, we have considered 2,3,4,5-tetrafluorobenzoic acid to form complexes with triorganotin. In this process, mixed-ligands (4,4'-bipy, triphenylphosphine oxide or phen) have been chosen as a co-ligand [6], because they are well known for their

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robustness to act as a spacer to unsaturated metal ion, which may facilitate the coordination between the metal ion and bulky organic molecules due to the minimization of crowding. In addition, these mixed ligands also have the ability to assemble into supramolecular framework with carboxyl group via intermolecular hydrogen bonds, π - π and C-H $\cdots\pi$ stacking interaction.

Herein, we synthesized several new triorganotin(IV) complexes with 2,3,4,5-tetrafluorobenzoic acid and mixed-ligands of the type: $R_3Sn(O_2CC_6HF_4)_m \cdot L$ ($m = 1$, $L = 0$, $R = Ph$ **1**; $m = 1$, $L = Ph_3PO$, $R = Ph$ **4**, Me **5**), $[R_3Sn(O_2CC_6HF_4)]_m \cdot L$ ($m = 2$, $L = 4,4'$ -bipy, $R = Ph$ **2**, Me **3**; $m = n$, $L = 0$, $R = Me$ **6**), and $[R_3Sn(O_2CC_6HF_4) \cdot (H_2O)]_m \cdot L \cdot C_2H_5OH$ ($m = 2$, $L = Phen$, $R = Ph$ **7**, Me **8**). All complexes were characterized by elemental, IR, 1H , ^{13}C and ^{119}Sn NMR spectra analyses. Except for **5** and **8**, all the complexes were also characterized by X-ray crystallography. All of these complexes show an intricate supramolecular organization in the solid state that results from a cumulative effect of intermolecular secondary interactions. The hydrogen bonds and aromatic interactions (π - π and C-H $\cdots\pi$) have been well documented [7].

2. Results and discussion

2.1. Syntheses

Reactions of triorganotin(IV) chloride and 2,3,4,5-tetrafluorobenzoic acid with the presence of mixed ligand of 4,4'-bipy, triphenylphosphine oxide or phen were carried out. The syntheses procedures are shown in Scheme 1.

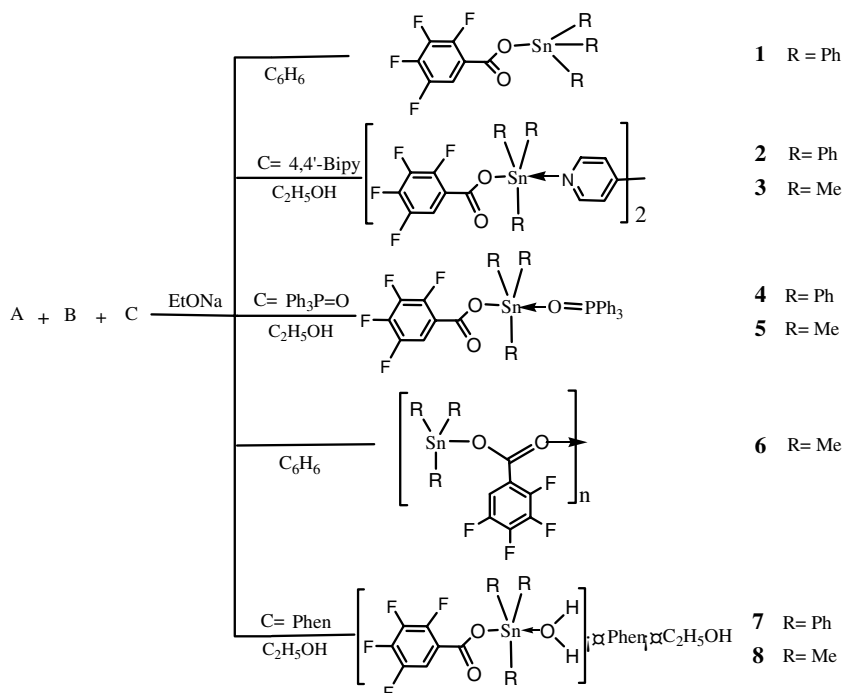
2.2. IR spectra

The stretching frequencies of interest are those associated with the C(O)O, Sn-C, Sn-O and Sn-N groups. The strong absorption in the region 468 – 496 cm^{-1} , which is absent in the spectrum of the free ligand, is assigned to the Sn-O stretching mode. All these values are consistent with those detected in number of organotin(IV)-oxygen derivatives [8].

In organotin carboxylate complexes, IR spectroscopy can provide useful information concerning the coordination mode of the carboxylate group. It was possible to distinguish the coordination mode of the $-CO_2$ group. In complex **6**, the magnitude of $\Delta\nu$ ($\Delta\nu = \nu_{as}(COO) - \nu_s(COO)$) of about 140 cm^{-1} , compared with those for the corresponding sodium salts, reveals that the carboxylate ligands function as bidentate ligands under the conditions employed [9]. While in other complexes, the value of $\Delta\nu$ of about 220 – 272 cm^{-1} , showing the carboxylate ligands are in a monodentate manner [10]. The $\nu(C=N)$ band, occurring at about 1523 cm^{-1} , is considerably shifted towards lower frequencies with respect to that of the free ligand, confirming the coordination of the heterocyclic N to the tin. This is also consistent with the X-ray diffraction study.

2.3. NMR spectra

The 1H NMR spectra show the expected integration and peak multiplicities. In the spectrum of the free ligand, the resonance observed at about 10.11 ppm, which is absent in the spectra of the complexes, indicates the replacement



Scheme 1. A=2,3,4,5-Tetrafluorobenzoic acid; B= Triorganotin(IV) chlorides.

of the carboxylic acid proton on complex formation. The chemical shifts of the signal for the methyl groups ($\delta = 0.61$ – 1.21 ppm) and the phenyl group ($\delta = 7.21$ – 7.76 ppm) appear at almost the same position as in the ligands. In addition, the resonance at 7.86–8.74 ppm are attributed to the protons of 4,4'-bipy and the resonance at 7.26–7.81 ppm are signed to the protons of phen [11].

In ^{13}C NMR spectra, the position of the carboxylate carbon moved to the lower field in all the complexes shifts, as compared with the ligand acid, indicating participation of the carboxylic group in coordination to tin(IV) [12]. Although at least two different types of carboxylate groups are present, only single resonances are observed for the COO group in the ^{13}C NMR spectra. These findings are interpreted by a fast equilibrium between bidentate and monodentate mode of COO groups of the complexes in CDCl_3 . It is noted that such an equilibrium explains that all carboxylate resonances are averaged out on the ^{13}C NMR time scales [13]. Complementary information for several complexes is given by the values of the coupling constant.

The ^{119}Sn NMR spectra of complex **1** show only one signal ($\delta = 86.3$ ppm), typical of a four-coordinate mode. However, the chemical shift for **2–8** ($\delta = -134.2$, -96.8 , -128.6 , -98.1 , -94.9 , -121.4 , -90.3 ppm, respectively), which are within the range corresponding to a typical five-coordinated species (-90 to -190), which is in accordance with their structures in the solid state [14].

2.4. Description of crystal structures

2.4.1. $[\text{Ph}_3\text{Sn}(\text{O}_2\text{CC}_6\text{HF}_4)]$ (**1**)

The molecular structure is illustrated in Fig. 1, selected bond distances and angles are listed in Table 1. The structure is in agreement with the result obtained from infrared spectroscopy and the lattice is comprised of discrete molecule of the complex. The coordination geometry about the

Sn atom is best described as distorted tetrahedral geometry defined by three *ipso*-C atoms of the phenyl groups and O(1) atom of the ligand. The bond length of Sn(1)–O(1) is 2.060(4) Å, which lies in the range of 2.038–2.115 Å that has been reported as the Sn–O covalent bond length [19], which proves that the oxygen atoms are coordinated to the tin atoms by a strong chemical bond. The relatively close interaction between O(2) and Sn(1) [$\text{Sn}(1)\cdots\text{O}(2) = 2.891(6)$ Å], which is in the range 2.634–2.916 Å. Although this distance is considerably longer than the normal Sn–O covalent bond length, they lie in range of Sn–O distances of 2.61–3.02 Å which have been confidently reported for intramolecular bonds [15]. The monodentate mode of coordination of the ligand is reflected in the disparate O(1)–C(1) and O(2)–C(1) bond distances of 1.302(8) and 1.200(9) Å,

Table 1
Selected bond lengths and angles for the complexes **1** and **2**

Complex 1		Complex 2	
Bond	Distance (Å)	Bond	Distance (Å)
Sn(1)–C(14)	2.104(6)	Sn(1)–C(20)	2.119(4)
Sn(1)–C(20)	2.122(7)	Sn(1)–C(8)	2.130(4)
Sn(1)–C(8)	2.124(6)	Sn(1)–C(14)	2.130(4)
Sn(1)–O(1)	2.060(4)	Sn(1)–O(1)	2.136(3)
O(1)–C(1)	1.302(8)	Sn(1)–N(1)	2.555(3)
O(2)–C(1)	1.200(9)		
Angle	Amplitude (°)	Angle	Amplitude (°)
C(14)–Sn(1)–C(8)	116.3(2)	C(20)–Sn(1)–C(8)	113.63(18)
C(14)–Sn(1)–C(20)	111.1(3)	C(20)–Sn(1)–C(14)	122.68(18)
C(20)–Sn(1)–C(8)	112.2(3)	C(8)–Sn(1)–C(14)	121.17(17)
C(14)–Sn(1)–O(1)	114.1(2)	C(20)–Sn(1)–O(1)	101.37(14)
C(8)–Sn(1)–O(1)	106.6(2)	C(14)–Sn(1)–O(1)	94.95(14)
C(20)–Sn(1)–O(1)	94.4(3)	C(20)–Sn(1)–N(1)	84.29(13)
C(1)–O(1)–Sn(1)	112.1(5)	C(8)–Sn(1)–N(1)	85.27(14)
O(2)–C(1)–O(1)	123.7(7)	C(14)–Sn(1)–N(1)	84.62(13)
		C(20)–Sn(1)–N(1)	158.45(15)
		O(1)–Sn(1)–N(1)	173.44(12)

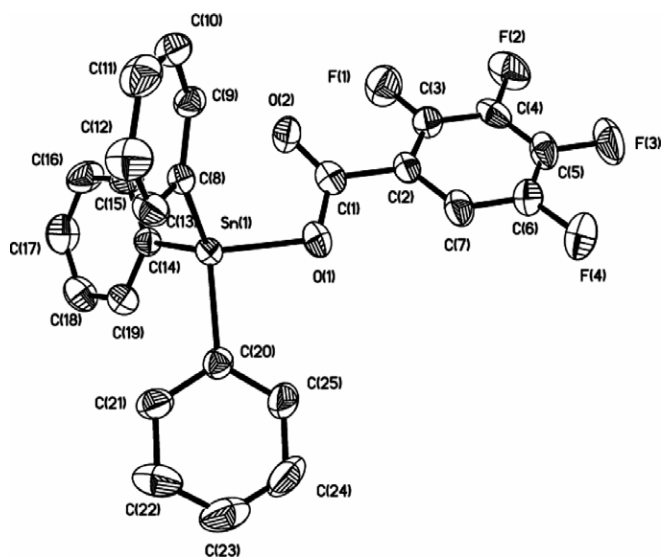


Fig. 1. Molecular structure of complex **1**.

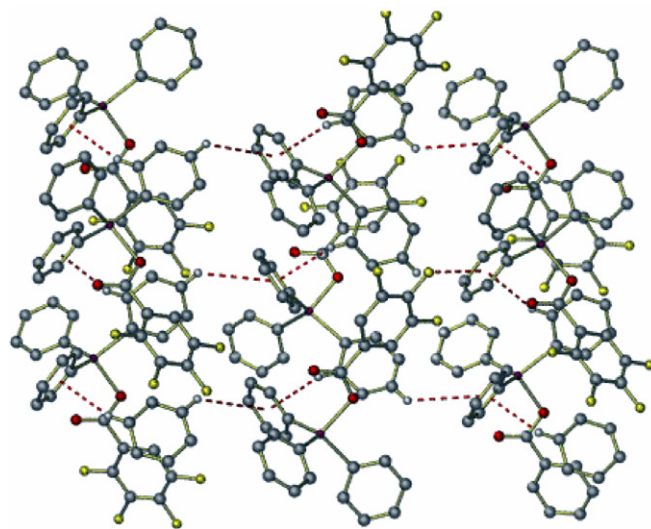


Fig. 2. Supramolecular structure of complex **1**, showing 2D framework via intermolecular C–H... π stacking interaction.

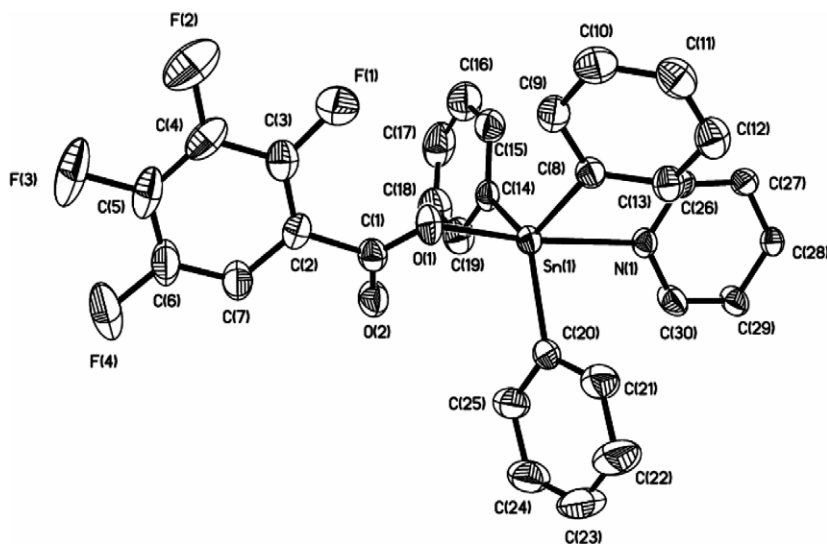


Fig. 3. Molecular structure of complex 2.

respectively, with the longer separation being associated with the stronger Sn(1)–O(1) interaction. These bond distances and angles are in agreement with the corresponding values found for similar Sn complexes contained in the Cambridge Structure Database [16]. The major distortion from the ideal geometry is found in the O(1)–Sn(1)–C(20) angle of 94.4(3)°, and the O(1)–Sn(1)–C(8) and O(1)–Sn(1)–C(14) are 106.6(2)° and 114.1(2)°, respectively. However, it is noteworthy that the C(8)–Sn(1)–C(14) angle of 116.3(2)° is the next major distortion from the ideal geometry.

The supramolecular structure of complex 1 is shown in Fig. 2, showing 2D framework by C–H··· π stacking interaction along *a* and *b* axis. It has been clearly established that this weak molecular force has a directional preference with the C–H pointing towards the center of the aromatic ring. The C(23)–H(23) atom is directed towards the symmetry related (1.5 – *x*, 0.5 + *y*, *z*) aromatic ring containing the C(8)A–C(13)A atoms. The closest contact of 2.843 Å occurs between the H(23)–C(8)A atoms. The distance of C(23)···Cg and H(23)···Cg are 3.598 Å and 2.673 Å, respectively. The angle of C(21)–H(21)···Cg is 135.53°. Another is the C(21)–H(21) atom, which is directed towards the symmetry related (0.5 + *x*, *y*, 1.5 – *z*) aromatic ring containing C(8)B–C(13)B atoms. The closest contact of 2.900 Å is H(21)–C(8)B atoms. The distance of C(21)···Cg and H(21)···Cg are 3.581 Å and 2.692 Å, respectively. The angle of C(21)–H(21)···Cg is 159.99°. These weak but significant stacking interactions stabilize these crystal structures.

2.4.2. $[Ph_3Sn(O_2CC_6HF_4)]_2 \cdot (4,4'-bipy)$ (2) and $[(CH_3)_3Sn(O_2CC_6HF_4)_2] \cdot (4,4'-bipy)$

The molecular structures of complexes 2 and 3 are shown in Figs. 3–5 selected bond distances and angles are listed in Tables 1 and 2. The asymmetric units of 2 and 3 are found to consist of one-half of the mononuclear mole-

cule, the remainder being generated by an inversion center at the midpoint of the co-crystallized 4,4'-bipy ligand. The structure contains two $R_3Sn(O_2CC_6HF_4)$ (*R* = Ph 2, Me 3) units associated through a bridging 4,4'-bipy moiety. The coordination environment around tin is five-coordinated distorted trigonal bipyramidal geometry with *trans*-NOSnR₃. The axial position was occupied by the carboxyl O atom of 2,3,4,5-tetrafluorobenzoic acid and the ring N atom of the neutral bipyridyl donor. The Sn(1)–O(1) bond length [2.136(3) Å] for 2 and [2.157(3) Å] for 3 is at the longer end of the range of Sn–O distances measured for monomeric triorganotin carboxylate.[17] The Sn–N bond length [2.555(3) Å] for 2 and [2.570(3) Å] for 3, closely to the Sn–N distance in $[Me_3Sn(PhN_2C_2S_3)]_2 \cdot (4,4'-bipy)$ [2.613(2) Å], [18] is longer than those found in organotin

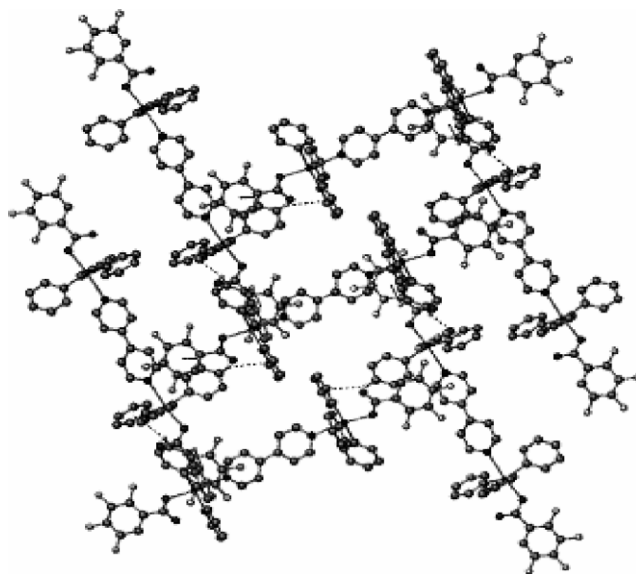


Fig. 4. Supramolecular structure of complex 2, showing 2D head-to-tail zigzag framework via intermolecular C–H··· π stacking interaction.

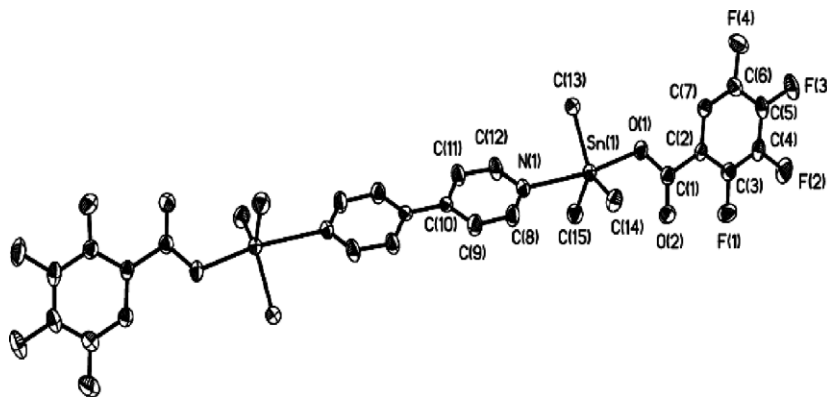


Fig. 5. Molecular structure of complex 3.

Table 2
Selected bond lengths and angles for the complexes 3 and 4

Complex 3		Complex 4	
Bond	Distance (Å)	Bond	Distance (Å)
Sn(1)–C(15)	2.121(4)	Sn(1)–C(14)	2.118(4)
Sn(1)–C(14)	2.123(4)	Sn(1)–C(20)	2.123(4)
Sn(1)–C(13)	2.129(4)	Sn(1)–C(8)	2.125(4)
Sn(1)–O(1)	2.157(3)	Sn(1)–O(1)	2.146(3)
Sn(1)–N(1)	2.570(3)	Sn(1)–O(3)	2.386(3)
O(1)–C(1)	1.295(4)		
O(2)–C(1)	1.213(4)		
C(10)–C(10)#1	1.476(6)		
Angle	Amplitude (°)	Angle	Amplitude (°)
C(15)–Sn(1)–C(14)	118.70(18)	C(14)–Sn(1)–C(8)	116.97(16)
C(15)–Sn(1)–C(13)	122.95(17)	C(14)–Sn(1)–C(20)	127.04(16)
C(14)–Sn(1)–C(13)	117.24(18)	C(20)–Sn(1)–C(8)	113.62(16)
C(15)–Sn(1)–O(1)	101.37(14)	C(14)–Sn(1)–O(1)	98.91(13)
C(14)–Sn(1)–O(1)	96.65(15)	C(8)–Sn(1)–O(1)	89.54(14)
C(13)–Sn(1)–O(1)	87.49(14)	C(20)–Sn(1)–O(3)	85.24(13)
C(15)–Sn(1)–N(1)	85.52(15)	C(20)–Sn(1)–O(1)	96.09(14)
C(14)–Sn(1)–N(1)	90.20(14)	C(8)–Sn(1)–O(3)	88.60(13)
C(13)–Sn(1)–N(1)	83.96(13)	O(1)–Sn(1)–O(3)	178.03(11)
O(1)–Sn(1)–N(1)	170.92(9)	P(1)–O(3)–Sn(1)	172.35(18)

tetrazoles [2.27–2.43 Å] [18]. It is noteworthy that a weak intramolecular Sn···O interaction is recognized between the Sn(1) and O(2) derived from the monodentate carboxyl group. The Sn(1)···O(2) distances of **2** and **3** are 3.086(3) Å and 3.058(3) Å, respectively, which are considerably less than the sum of the van der Waals radii (3.68 Å) [20]. Thus, if the weak Sn(1)···O(2) interaction is considered, the geometry of Sn(1) is best described as distorted octahedron. Furthermore, owing to the coordination of N atom, the angles of O–Sn–C [94.95(14)–101.37(14)°] for **2** and [87.49(14)–96.65(15)°] for **3**, is smaller than those of [Ph₃Sn(O₂CC₆HF₄)] [94.95(3)–14.1(2)°] in complex **1**. The angle of O–Sn–N and C–Sn–C are 173.44(12)° and [113.63(18)–122.68(18)°] in complex **2** and 170.92(9)° and [117.24(18)–122.95(17)°] in complex **3**, which reflect this coordination geometry.

In Fig. 4, the supramolecular structure of complex **2** exhibits a 2D zigzag structure via intermolecular edge-

to-face C–H···π stacking interaction. Every pair of adjacent C–H atom are directed towards the symmetry related (C(11)–H(11)···Cg = 3.808 Å, C(12)–H(12)···Cg = 4.062 Å, symmetry operation: 1 – x, –0.5 + y, 0.5 – z) aromatic rings and formed head-to-tail zigzag chain structure, which are further connected by C–H···π stacking interaction into a 2D structure.

The supramolecular frameworks of complex **3** are shown in Fig. 6a,b. The 1D ladder-like chain structures and alternation of moleculars are easily recognized, which were assembled by two distinct intermolecular C–H···O and C–H···F hydrogen bonds with the distances of 2.462 Å and 2.648 Å and angles of 149.90° and 126.67°, which are consistent with what have been reported in the Cambridge database [20]. The ladders are hydrogen-bonded into continuous parallelogram lattices, which form two infinite 1D chains with the bipyridyl rings along *a*-axis.

2.4.3. [Ph₃Sn(O₂CC₆HF₄)] · OPPh₃ (**4**)

The molecular structure is shown in Fig. 7, selected bond distances and angles are listed in Table 2. The geometry at central Sn atoms is slightly distorted trigonal bipyramid with Ph₃PO coordinated in a *trans* position to the oxo ligand, in which three C atoms of phenyl groups form the equatorial plane, the sum of the trigonal plane angle is 357.63(16)°, while two oxygen atoms from the carboxyl groups and Ph₃PO ligand occupy the axial apical position. The Sn(IV) atom is displaced from the equatorial plane of the coplanar atoms toward the oxo atom O(3) by 0.0707 Å and the slightly distortion lies the angle of O(1)–Sn(1)–O(3) [178.03(11)°]. Moreover, the bond distance of O(1)–Sn(1) is 2.146(3) Å, larger than the O(1)–Sn(1) [2.060(4) Å] in complex **1** owing to electrostatic repulsion of the phenyl groups to O(1) atom. The geometry of the Ph₃PO ligand shows no usual features. The P–O bond, 1.460(1) Å in free Ph₃PO [21], is only slightly affected by the coordination to Sn atom (1.486(3) Å). The phosphorus atoms show tetrahedral coordination, being surrounded by the atoms C(32), C(38), C(26) and O(3). The tetrahedral angles vary from 106.67(19)° to 107.91(19)°. The P–C bond lengths are basal the same [(1.798 ± 0.004) Å].

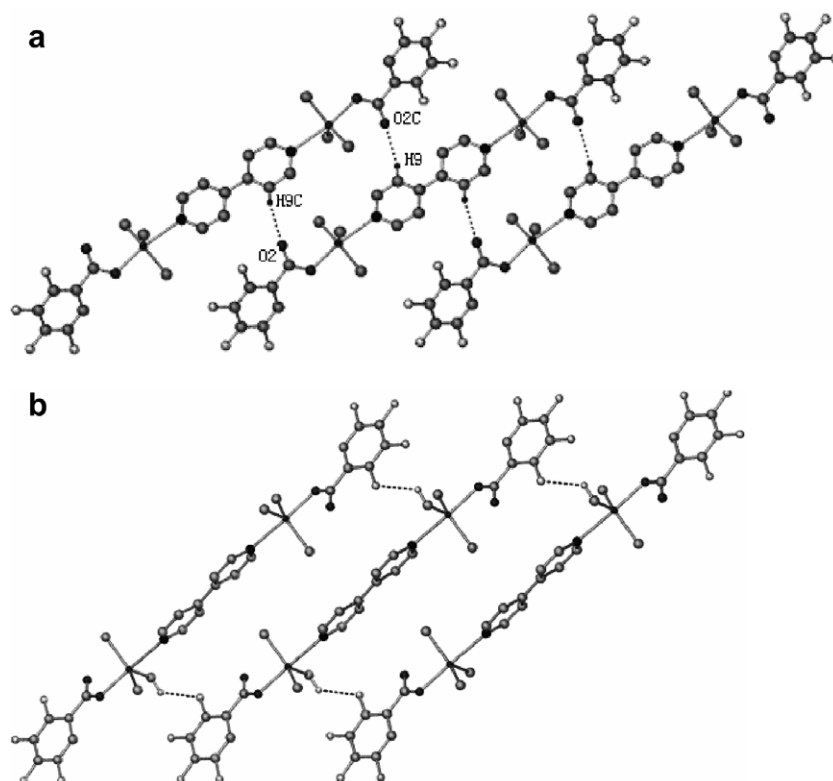


Fig. 6. Supramolecular frameworks of complex 3, showing 1D infinite chain structures by C–H···O (a) and C–H···F hydrogen bonds (b).

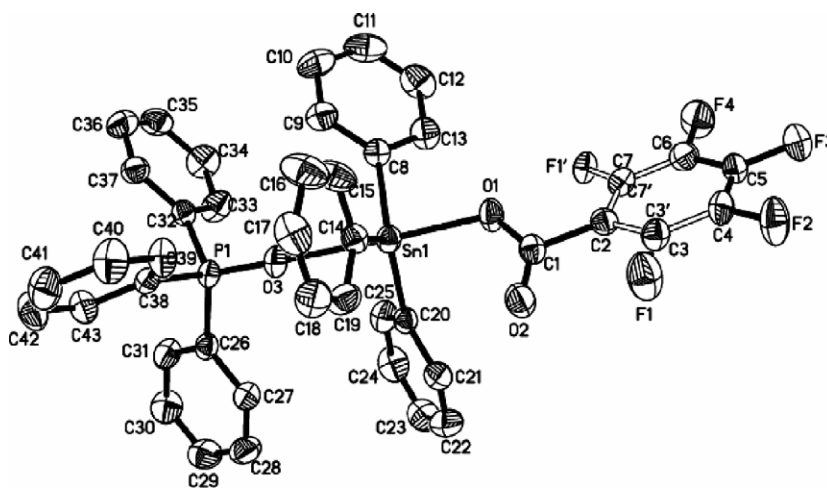


Fig. 7. Molecular structure of complex 4.

The supramolecular structure unit of complex 4 exists two distinct C–H···F hydrogen bonds [C(11)–H(11B)···F(2AA), 2.657, 3.152 Å and 121.77°; C(29)–H(29)···F(1'B), 2.595, 3.465 Å and 156.01°] and formed a box-like ring structure (Fig. 8). Further, these rings were assembled into 2D network structure.

2.4.4. $[(CH_3)_3Sn(O_2CC_6HF_4)]_n$ (6)

The molecular structure of complex 6 is shown in Fig. 9, selected bond lengths and angles are listed in Table 3. In the crystalline state, complex 6 adopts an infinite zigzag 1D polymeric chain structure with a five-coordinated tin

center, which is generated by the bidentate bridging carboxylate ligands and the Sn center. The Sn atom exists in a distorted trigonal bipyramidal environment with two O atoms and three methyl groups, which exhibits a *trans*- R_3SnO_2 geometry. The axial positions are occupied by O(1) and O(3) and axial angle is 173.98(13)°. The sum of C–Sn–C is 357.3(3)°, which illustrates the three methyl groups and Sn atom are nearly coplanar.

The deviation only slightly from regular distorted geometry, mean deviation from plane is 0.0746(3) Å. A evident twist is shown between this COO group and the aromatic ring [O(1)/C(1)/C(2)/C(3) is –44.51° and O(2)/C(1)/C(2)/

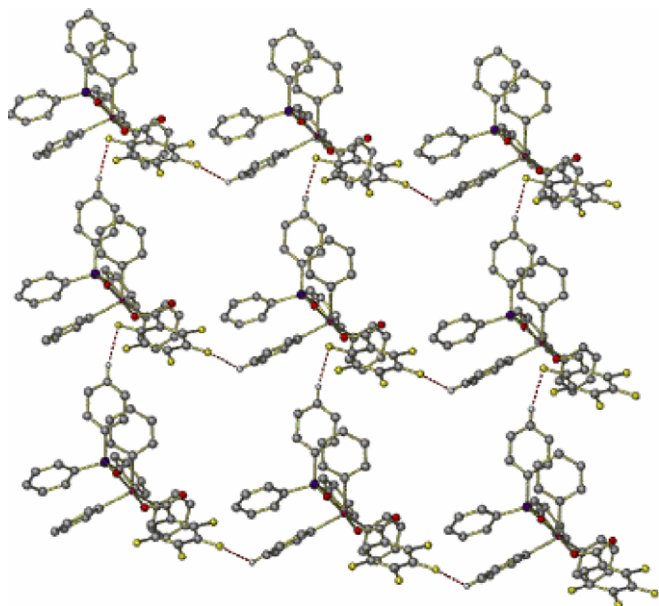


Fig. 8. 2D network structure of complex 4, formed through intermolecular C–H···F hydrogen bonds.

C(7) is -43.54°]. The disparity in the Sn–O distance is reflected in the associated C–O distances, the longer C–O bond involving the O(1) atom with the shorter Sn–O interaction. The unit cell (Fig. 10 and 11) exhibits a elliptic macrocycle in every layer of the supramolecular structure. An elliptic channel was formed via the stacking interaction along *c*-axis direction.

In Fig. 12a, one-dimensional polymeric chain structure are interconnected by means of π – π stacking interactions between the parallel phenyl groups (dihedral angle is 0°) to form a paratactic double-chain structure. The two phenyl

Table 3
Selected bond lengths and angles for the complexes 6 and 7

Complex 6		Complex 7	
Bond	Distance (Å)	Bond	Distance (Å)
Sn(1)–C(15)	2.096(6)	Sn(1)–C(14)	2.123(4)
Sn(1)–C(17)	2.098(6)	Sn(1)–C(20)	2.127(5)
Sn(1)–C(16)	2.109(6)	Sn(1)–C(8)	2.129(5)
Sn(1)–O(3)	2.161(3)	Sn(1)–O(1)	2.187(3)
Sn(2)–C(20)	2.099(6)	Sn(1)–O(3)	2.351(3)
Sn(2)–C(19)	2.107(6)		
Sn(2)–C(18)	2.117(6)		
Sn(2)–O(2)	2.170(4)		
Sn(2)–O(4)#1	2.587(4)		
O(4)–Sn(2) #2	2.587(4)		
Angle	Amplitude ($^\circ$)	Angle	Amplitude ($^\circ$)
C(15)–Sn(1)–C(17)	117.9(3)	C(20)–Sn(1)–C(8)	115.62(19)
C(15)–Sn(1)–C(16)	116.3(3)	C(20)–Sn(1)–C(14)	120.24(18)
C(17)–Sn(1)–C(16)	123.1(3)	C(8)–Sn(1)–C(14)	123.32(18)
C(15)–Sn(1)–O(3)	90.5(2)	C(20)–Sn(1)–O(1)	95.48(15)
C(17)–Sn(1)–O(3)	98.6(2)	C(14)–Sn(1)–O(1)	96.60(15)
C(20)–Sn(2)–C(19)	124.8(3)	C(20)–Sn(1)–O(3)	90.05(15)
C(20)–Sn(2)–C(18)	115.8(3)	C(8)–Sn(1)–O(3)	86.07(15)
C(19)–Sn(2)–C(18)	117.2(3)	O(3)–Sn(1)–O(1)	172.42(12)
O(2)–Sn(2)–O(4)#1	175.0(15)	C(14)–Sn(1)–O(3)	85.01(14)

rings involved in this π – π stacking are staggered with an interplanar distance of 3.700 Å (symmetry operation $2 - x, 1 - y, 1 - z$) and departure angle of phenyl–phenyl is 15.6° . The polymeric chain are further π -stacked to form a two-dimensional framework.

In Fig. 12b, the supramolecular structure exhibits a 2D network structure. The resultant C–H···F contacts allow the molecular to arrange into a staircase type of one-dimensional polymeric chain array in the solid state. The distances of paratactic two C–H···F interactions are

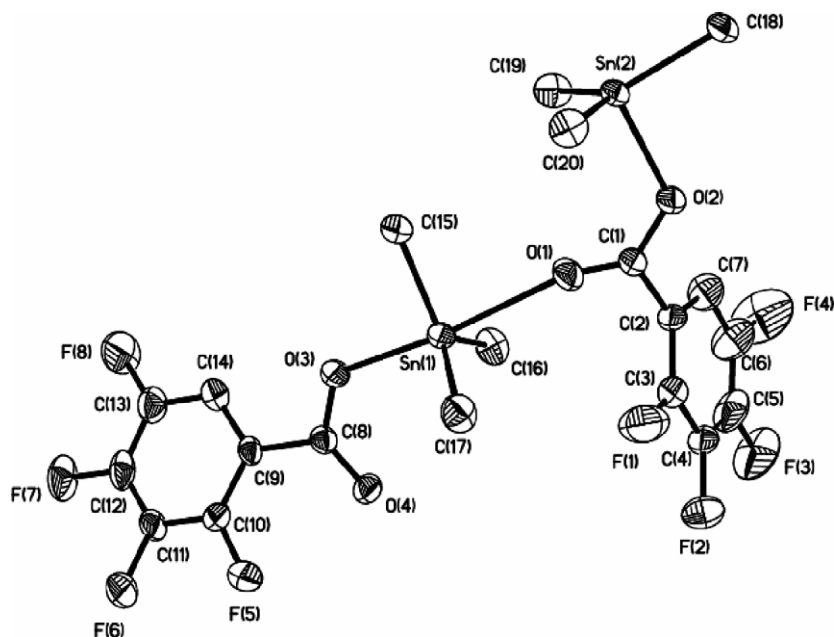


Fig. 9. Molecular structure of complex 6.

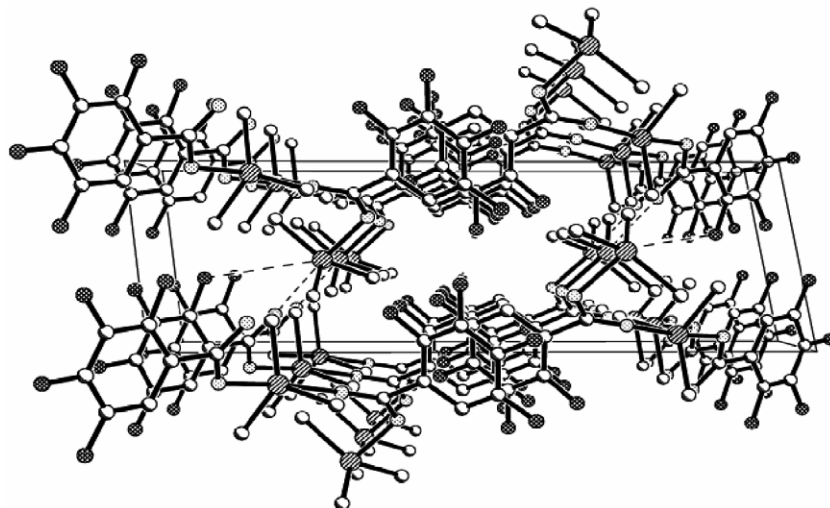


Fig. 10. Cell packing of complex **6**, showing a multi-membered elliptic macrocycle in every layer and a channel-like framework via O...Sn and non-bonded F...Sn interaction.

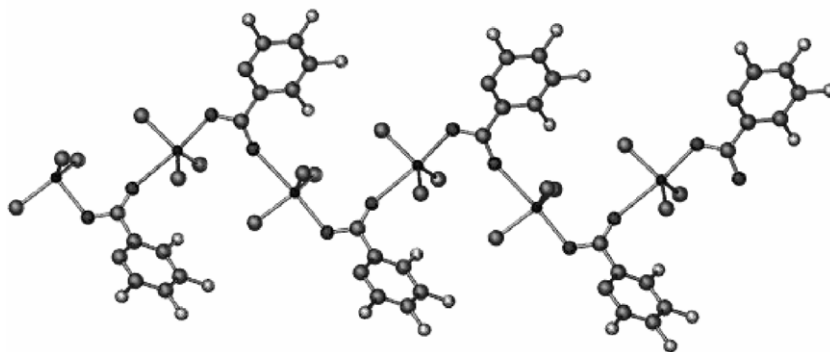


Fig. 11. Supramolecular structure of complex **6**, showing 1D zigzag chain via intermolecular O → Sn coordinating.

equivalent of 2.589 Å (symmetry operation $1 - x, 2 - y, -z$). These interactions together with the polymeric chain assemble into a macrocycle quadrate lattice unit [the angle O(1)–Sn(1)/ O(2)–Sn(2) is 91.5°].

2.4.5. $[Ph_3Sn(O_2CC_6HF_4) \cdot (OH_2)_2]_2 \cdot (phen)_2$ (**7**)

For complex **7**, co-crystallized phen and two monomers of the main component, $[Ph_3Sn(O_2CC_6HF_4) \cdot H_2O]$, are found in the crystal in Fig. 13, selected bond lengths and angles are listed in Table 3. In the two monomers, the geometries at Sn(1) is distorted trigonal bipyramidal with O(3) from the water molecular and O(1) from carboxyl group coordinating to Sn atom and occupying the axial apical position. The sum of the trigonal plane angles is 359.18°, which illustrates Sn(1), C(8), C(14) and C(20) are almost coplanar with the tin atom slightly deviating from the ideal plane by 0.0420 Å. Distortion from strict trigonal bipyramidal coordination lies to the angle of O(1)–Sn(1)–O(3) [172.42(12)°]. There is only one monodentate type of carboxyl group in the monomers. The guest water molecular is also found in the coordination sphere, with Sn–O bond lengths of 2.351(3) Å, comparable in strength to the

intermolecular tin–oxygen bonds and close in length to the sum of covalent radii of tin and oxygen (2.13 Å), which is recognized as strongly coordinative bonds. Worth mentioning here is that bond length of O(1) and Sn(1) is 2.187(3) Å, which is larger than that of O(1)–Sn(1) (2.060(4) Å) in the complex **1**, owing to electrostatic repulsion of the phenyl groups to O(1) atom.

In Fig. 14, the dimer of complex **7** with centrosymmetric 14-membered ring and *trans* carboxyl ligand is formed through the hydrogen bonds from the water molecular to the nitrogen atom of its heterocycle (O...N = 2.785(5) Å), and another (O...N = 2.797(5) Å) to the nitrogen atom of the symmetrical *o*-phenanthroline molecular. The two pairs of hydrogen bonds hold together the flat heterocyclic bases [22], which are twisted with respect to each other in a propeller-like conformation. The hydrogen bonding distances exceed those found in aquachlorotriphenyl tin 3,4,7,8-tetramethyl-*O*-phenanthroline (O...N = 2.661(3), 2.767(3) Å; N...O...N = 60.9(1)°), whose five-membered C–N...O water...N–C ring is planar (\sum angles = 540(1)°) [23]. The packing appears to be less efficient compared with that of the title complex, as suggested by its density (1.475 g cm⁻³).

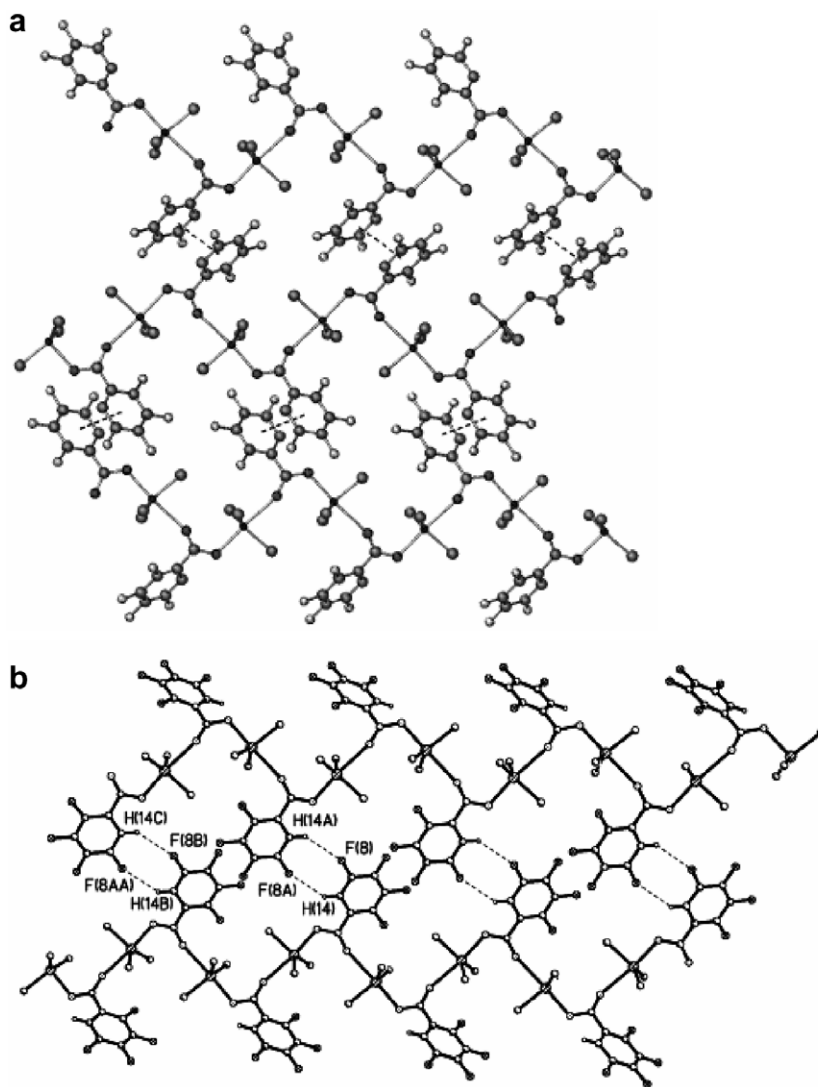


Fig. 12. Supramolecular structure of complex 6: (a) showing 1D framework via interchain π - π stacking interaction and (b) showing a staircase type of one-dimensional polymer chain array via interchain C-H...F hydrogen bonds.

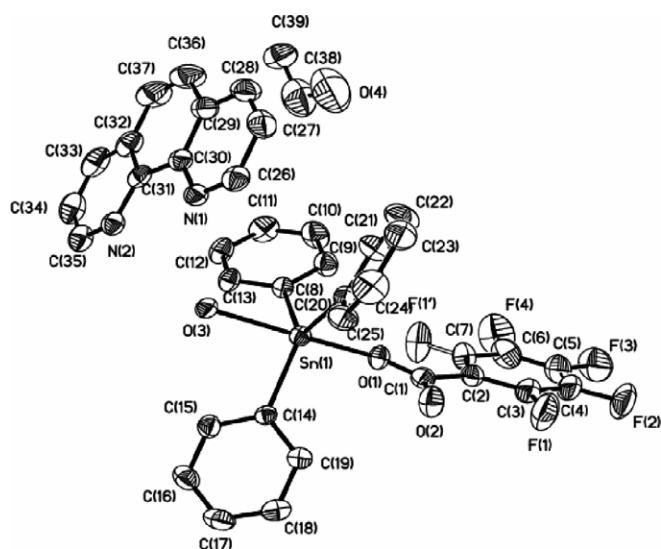


Fig. 13. Molecular structure of complex 7.

In this complex, hydrogen bonding involves only the two outer pyridyl groups of the non-planar terpyridyl ligand [24].

As shown in Fig. 15, these dimer structure units are assembled by intermolecular C-H...F hydrogen bond and formed a linear 1D chain structure with multi-membered squareness parallelogrammatic organotin rings in the defined plane. The distance of C-H36A...F2AB and C-H36D...F2 is 2.633 Å, which is somewhat smaller than the sum of van der Waals radii (2.67 Å) [20]. The corresponding angle is 142.64°, which is consistent with those reported by Dautel [25]. These adjacent 1D chain structures are further self-assembled via π - π (face-to-face) stacking interaction and formed a 2D network framework (Fig. 16). The average separation between the two ring is 3.60 Å and the dihedral angle is 0°, which illustrated two completely parallel aromatic rings. The angle between centric linkage and the perpendicular of phenyl rings is 3.2°, showing the slightly derivation between phenyl rings.

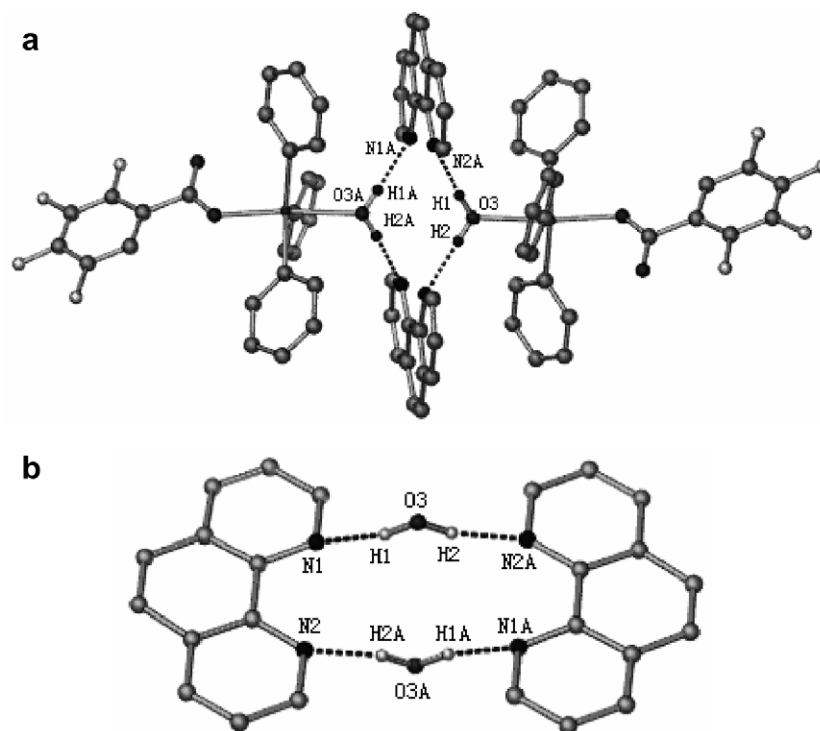


Fig. 14. The dimer structure of complex 7 (a) showing a 14-membered ring (b) via O–H···N hydrogen bond.

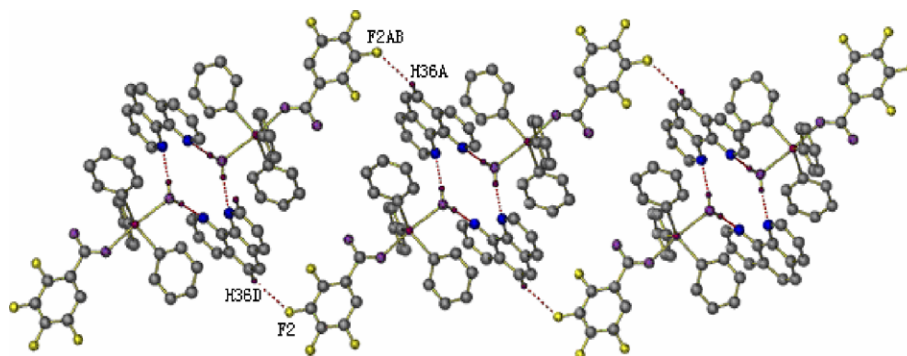


Fig. 15. The one-dimensional chain structure of complex 7 with multi-membered squareness ring via C–H···F hydrogen bond.

2.5. Conclusion

In summary, a series of triorganotin (IV) complexes based on 2,3,4,5-tetrafluorobenzoic acid have been synthesized and characterized. In general, trimethyltin benzoates mainly assume one-dimensional associated arrangements (such as complex **6**), and triphenyltin benzoates generally exist in a discrete five-coordinate form (complexes **2**, **4**, and **7**). However, complexes **1** and **3** are different with **1** containing a four-coordinated tetrahedron geometry and **3** containing two mononuclear molecular units associated through a bridging 4,4'-bipy. Furthermore, these structures are able to assemble into supramolecular framework through hydrogen bonds and π – π or C–H··· π stacking interaction. In general, in the crystalline state these complexes generally adopted either a polymeric structure with a five-coordinate tin

atom or a discrete four- or five-coordinate form. The supramolecular chemistry showed intriguing structural topologies and their 1D or 2D framework was formed through the self-assembly based on covalent interactions or supramolecular contacts (such as hydrogen bonding or stacking interactions).

3. Experimental details

3.1. Materials and measurements

Trimethyltin chloride, triphenyltin chloride, 2,3,4,5-tetrafluorobenzoic acid, 4,4'-bipy, triphenylphosphine oxide and phen are commercially available and were used without further purification. The melting points were obtained with Kofler micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet-460 spectro-

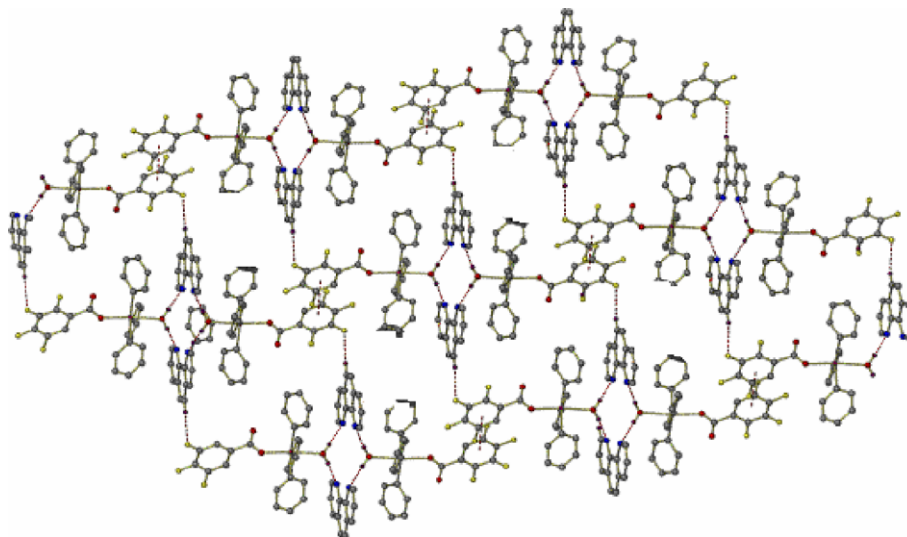


Fig. 16. Supramolecular structure of complex **7**, showing 2D planar framework via intermolecular C–H···F hydrogen bonding and C–H··· π stacking interaction.

photometer using KBr discs and sodium chloride optics. ^1H and ^{13}C NMR spectra were recorded on Varian Mercury Plus 400 spectrometer operating at 400, 100.6, and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. Elemental analyses were performed with a PE-2400II apparatus.

3.2. Syntheses

3.2.1. $[\text{Ph}_3\text{Sn}(\text{O}_2\text{CC}_6\text{HF}_4)]$ (**1**)

The reaction was carried out under nitrogen atmosphere. 2,3,4,5-Tetrafluorobenzoic acid (0.194 g, 1 mmol) and sodium ethoxide (0.276 g, 1.2 mmol) were added to the solution of dry benzene in a Schlenk flask and stirred for 0.5 h. Triphenyltin chloride (0.385 g, 1 mmol) was then added to the reactor and the reaction mixture was stirred for 12 h at 40 °C. After filtration, the solvent was evaporated in vacuo. The solid was recrystallized from ether/petroleum. Colorless crystal was obtained. Yield: 76%; m.p. 102–104 °C (dec.). Anal. Calc. for $\text{C}_{25}\text{H}_{16}\text{F}_4\text{O}_2\text{Sn}_2$: C, 55.29; H, 2.97. Found: C, 55.48; H, 2.76%. IR (KBr, cm^{-1}): $\nu_{\text{asym}}(\text{COO})$ 1641, $\nu_{\text{sym}}(\text{COO})$ 1382, $\nu(\text{Sn}-\text{C})$, 559, $\nu(\text{Sn}-\text{O})$, 449. ^1H NMR (CDCl_3 , ppm): δ 7.50–7.71 (m, 1H), δ 7.48–7.82 (m, 15H). ^{13}C NMR (CDCl_3 , ppm): δ 167.2, 137.5, 136.5, 130.6, 129.4, 114.3. ^{119}Sn NMR (CDCl_3): –86.3 ppm.

3.2.2. $[\text{Ph}_3\text{Sn}(\text{O}_2\text{CC}_6\text{HF}_4)]_2 \cdot (4,4'\text{-bipy})$ (**2**)

Complex **2** was prepared in the same way as that of complex **1** except that excess 4,4'-bipy was added to the mixture. The solid was then recrystallized from ether/petroleum. Yield: 81%; m.p. 140–142 °C. Anal. Calc. for $\text{C}_{60}\text{H}_{40}\text{F}_8\text{N}_2\text{O}_4\text{Sn}_2$: C, 58.01; H, 3.24; N, 2.35. Found: C, 58.38; H, 3.08; N, 2.16%. IR (KBr, cm^{-1}): $\nu_{\text{asym}}(\text{COO})$ 1648, $\nu_{\text{sym}}(\text{COO})$ 1428, $\nu(\text{Sn}-\text{C})$ 557, $\nu(\text{Sn}-\text{O})$ 533, $\nu(\text{Sn}-\text{N})$ 456. ^1H NMR (CDCl_3 , ppm): δ 7.53–7.72 (m, 2H,

Ph–H), δ 7.41–7.79 (m, 30H), 8.70–8.73 (d, $J_{\text{H,H}} = 9.6$ Hz, 8H). ^{13}C NMR (CDCl_3 , ppm): δ 150.9, 145.8, 137.4, 136.9, 130.7, 129.3, 128.9, 121.6, 113.3. ^{119}Sn NMR (CDCl_3): –134.2 ppm.

3.2.3. $[(\text{CH}_3)_3\text{Sn}(\text{O}_2\text{CC}_6\text{HF}_4)_2] (4,4'\text{-bipy})$ (**3**)

Complex **3** was prepared in the same way as that of complex **1** except that excess 4,4'-bipy was added to the mixture. The solid was then recrystallized from ether/petroleum. Yield: 76%; m.p. 134–136 °C. Anal. Calc. for $\text{C}_{30}\text{H}_{10}\text{F}_8\text{N}_2\text{O}_4\text{Sn}_2$: C, 42.30; H, 1.18. N, 2.25. Found: C, 42.53; H, 1.26; N, 2.08%. IR (KBr, cm^{-1}): $\nu_{\text{asym}}(\text{COO})$ 1656; $\nu_{\text{sym}}(\text{COO})$ 1384; $\nu(\text{Sn}-\text{C})$ 528; $\nu(\text{Sn}-\text{O})$ 498; $\nu(\text{Sn}-\text{N})$ 454. ^1H NMR (CDCl_3 , ppm): 7.48–7.62 (m, 2H, Ph–H), 8.73–8.75 (m, 8H, N–H), 0.61–0.76 (m, 9H). ^{13}C NMR (CDCl_3 , ppm): 152.1, 148.9, 146.6, 144.3, 143.8, 141.4, 15.3 (CH_3). ^{119}Sn NMR (CDCl_3): –96.8 ppm.

3.2.4. $\text{Ph}_3\text{Sn}(\text{O}_2\text{CC}_6\text{HF}_4)] \cdot \text{OPPh}_3$ (**4**)

Complex **4** was prepared in the same way as that of complex **1**, except that excess triphenylphosphine oxide was added to the mixture. The solid was then recrystallized from ether/petroleum. Yield: 75%; m.p. 161–163 °C. Anal. Calc. for $\text{C}_{43}\text{H}_{31}\text{F}_4\text{O}_3\text{PSn}$: C, 62.88; H, 3.80. Found: C, 62.65; H 3.98%. IR (KBr, cm^{-1}): $\nu_{\text{asym}}(\text{COO})$ 1662, $\nu_{\text{sym}}(\text{COO})$ 1437, $\nu(\text{Sn}-\text{C})$ 540, $\nu(\text{Sn}-\text{O})$ 454. ^1H NMR (CDCl_3 , ppm): δ 7.47–7.68 (m, 1Ph–H), δ 7.42–7.80 (m, 15H), 8.70–8.72 (m, 8N–H). ^{13}C NMR (CDCl_3 , ppm): δ 138.0, 137.6, 136.5, 132.9, 132.0, 131.8, 129.0, 128.6, 113.8. ^{119}Sn NMR (CDCl_3): –128.6 ppm.

3.2.5. $[(\text{CH}_3)_3\text{Sn}(\text{O}_2\text{CC}_6\text{HF}_4)] \cdot \text{OPPh}_3$ (**5**)

Complex **5** was prepared in the same way as that of complex **1** except that excess 4,4'-bipy was added to the mixture. The solid was then recrystallized from ether/petroleum. Yield: 81%; m.p. 140–142 °C. Anal. Calc. for $\text{C}_{28}\text{H}_{25}\text{F}_4\text{O}_3\text{PSn}$: C, 52.95; H, 3.97. Found: C, 52.69; H,

4.08%. IR (KBr, cm^{-1}): $\nu_{\text{asym}}(\text{COO})$ 1621; $\nu_{\text{sym}}(\text{COO})$ 1376; $\nu(\text{P}=\text{O})$ 1168; $\nu(\text{Sn}-\text{C})$ 535; $\nu(\text{Sn}-\text{O})$ 452. ^1H NMR (CDCl_3 , ppm): δ 7.47–7.80 (m, 1H, Ph-H), δ 7.41–7.78 (m, 15H). ^{13}C NMR (CDCl_3 , ppm): δ 137.8, 136.7, 136.4, 132.6, 132.0, 131.7, 130.2, 129.5, 113.6, 14.8 (CH_3). ^{119}Sn NMR (CDCl_3): -98.1 ppm.

3.2.6. $[(\text{CH}_3)_3\text{Sn}(\text{O}_2\text{CC}_6\text{HF}_4)_2]_n$ (**6**)

Complex **6** was prepared in the same way as that of complex **1**, the solid was recrystallized from ethanol. Yield: 81%; m.p. 108–110 °C. Anal. Calc. For $\text{C}_{20}\text{H}_{20}\text{F}_8\text{O}_4\text{Sn}_2$: C, 33.65; H, 2.82. Found: C 33.32, H 2.97%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{C}=\text{O})$ 1615, $\nu_{\text{s}}(\text{C}-\text{O})$ 1475, $\nu_{\text{as}}(\text{Sn}-\text{C})$ 555, $\nu_{\text{s}}(\text{Sn}-\text{C})$ 524, $\nu(\text{Sn}-\text{O})$ 483. ^1H NMR (CDCl_3 , ppm): δ 7.56–7.67 (m, 2H, Ph-H), δ 0.50–1.26 (m, 18H). ^{13}C NMR (CDCl_3 , ppm): 166.1, 149.2, 147.4, 146.7, 144.9, 142.4, 140.0, 139.7, 14.6 (CH_3). ^{119}Sn NMR (CDCl_3): -94.9 ppm.

3.2.7. $[\text{Ph}_3\text{Sn}(\text{O}_2\text{CC}_6\text{HF}_4) \cdot (\text{OH}_2)]_2 \cdot (1,10\text{-Phen})_2 \cdot \text{C}_2\text{H}_5\text{OH}$ (**7**)

Complex **7** was prepared in the same way as that of complex **1** except that excess 1,10-Phen was added to the mixture. The solid was then recrystallized from ether/petroleum. Yield: 81%; m.p. 140–142 °C. Anal. Calc. for $\text{C}_{76}\text{H}_{58}\text{F}_8\text{N}_4\text{O}_7\text{Sn}_2$: C, 59.71; H, 3.82; N, 3.66. Found: C, 59.42; H, 3.67; N, 3.82%. IR (KBr, cm^{-1}): $\nu_{\text{asym}}(\text{COO})$ 1664, $\nu_{\text{sym}}(\text{COO})$ 1425, $\nu(\text{Sn}-\text{C})$ 523, $\nu(\text{Sn}-\text{O})$ 454. ^1H

NMR (CDCl_3 , ppm): δ 9.20 (s, $\text{C}_{10}\text{H}_8\text{N}_2$), δ 8.26 (d, $J_{\text{H,H}} = 5.8$ Hz, 4H, $\text{C}_{10}\text{H}_8\text{N}_2$), δ 7.47–7.70 (m, 1H, Ph-H), δ 7.41–7.87 (m, 15H). ^{13}C NMR (CDCl_3 , ppm): δ 150.3, 145.8, 137.4, 136.9, 130.5, 129.4, 128.7, 126.5, 123.0, 114.1. ^{119}Sn NMR (CDCl_3): -121.4 ppm.

3.2.8. $[(\text{CH}_3)_3\text{Sn}(\text{O}_2\text{CC}_6\text{HF}_4) \cdot (\text{OH}_2)]_2 \cdot (1,10\text{-phen})_2 \cdot \text{C}_2\text{H}_5\text{OH}$ (**8**)

Complex **8** was prepared in the same way as that of complex **1** except that excess 1,10-phen was added to the mixture. The solid was then recrystallized from ether/petroleum. Yield: 81%; m.p. 140–142 °C. Anal. Calc. for $\text{C}_{46}\text{H}_{46}\text{F}_8\text{N}_2\text{O}_4\text{Sn}_2$: C, 51.14; H, 4.29; N, 2.59. Found: C, 51.38; H, 4.36; N, 2.42%. IR (KBr, cm^{-1}): $\nu_{\text{asym}}(\text{COO})$ 1659, $\nu_{\text{sym}}(\text{COO})$ 1392, $\nu(\text{Sn}-\text{C})$ 542, $\nu(\text{Sn}-\text{O})$ 461. ^1H NMR (CDCl_3 , ppm): δ 7.48–7.71 (m, 1H, Ph-H), δ 7.45–7.81 (m, 15H), δ 9.12 (s, $\text{C}_{10}\text{H}_8\text{N}_2$), δ 8.42 (d, $J_{\text{H,H}} = 6.4$ Hz, 4H, $\text{C}_{10}\text{H}_8\text{N}_2$). ^{13}C NMR (CDCl_3 , ppm): δ 150.8, 145.8, 137.4, 136.9, 130.6, 129.6, 128.9, 121.7, 113.5, 113.3, 14.2 (CH_3). ^{119}Sn NMR (CDCl_3): -90.3 ppm.

3.3. X-ray crystallography

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart-1000 CCD area-detector with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). A semi-empirical absorption

Table 4
Crystal, data collection and structure refinement parameters of complexes 1–3

Complexes	1	2	3
Empirical formula	$\text{C}_{25}\text{H}_{16}\text{F}_4\text{O}_2\text{Sn}$	$\text{C}_{60}\text{H}_{40}\text{F}_8\text{N}_2\text{O}_4\text{Sn}_2$	$\text{C}_{30}\text{H}_{10}\text{F}_8\text{N}_2\text{O}_4\text{Sn}_2$
Formula weight	543.07	1242.32	851.78
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	<i>Pbca</i>	<i>P2(1)/c</i>	<i>P1</i>
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	10.845(2)	10.388(2)	7.003(6)
<i>b</i> (Å)	18.442(4)	13.809(3)	8.945(8)
<i>c</i> (Å)	22.301(5)	18.865(4)	13.410(11)
α (°)	90	90	90.090(11)
β (°)	90	96.952	98.876(11)
γ (°)	90	90	96.183(11)
<i>V</i> (Å ³)	4460.3(17)	2686.0(11)	825.0(12)
<i>Z</i>	8	2	1
<i>D</i> _{calc} (Mg m ⁻³)	1.617	1.536	1.715
<i>F</i> (000)	2144	1236	408
μ (mm ⁻¹)	1.198	1.006	1.594
Crystal size (mm)	0.45 × 0.38 × 0.29	0.48 × 0.46 × 0.40	0.48 × 0.40 × 0.36
θ Range	1.83–25.00	2.18–25.01	2.74–28.26
Index ranges	$-12 \leq h \leq 12$ $-15 \leq k \leq 21$ $-26 \leq l \leq 26$	$-11 \leq h \leq 12$ $-15 \leq k \leq 16$ $-22 \leq l \leq 22$	$-6 \leq h \leq 9$ $-11 \leq k \leq 11$ $-17 \leq l \leq 17$
Reflections collected	22,046	13,842	5131
Unique reflections (<i>R</i> _{int})	3925 (0.0671)	4729 (0.0387)	3722 (0.0195)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max/min transmission	0.7227, 0.6147	0.6890, 0.6437	0.5976, 0.5149
Data, restraints, parameters	3925, 0, 289	4729, 0, 343	3722, 0, 208
GOF	1.004	1.002	1.000
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0419, <i>wR</i> ₂ = 0.0966	<i>R</i> ₁ = 0.0345, <i>wR</i> ₂ = 0.0828	<i>R</i> ₁ = 0.0318, <i>wR</i> ₂ = 0.0777
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0929, <i>wR</i> ₂ = 0.1297	<i>R</i> ₁ = 0.0596, <i>wR</i> ₂ = 0.1012	<i>R</i> ₁ = 0.0398, <i>wR</i> ₂ = 0.0843

Table 5
Crystal data collection and structure refinement parameters of complexes **4**, **6** and **7**

Complexes	4	6	7
Empirical formula	C ₄₃ H ₃₁ F ₄ O ₃ PSn	C ₂₀ H ₂₀ F ₈ O ₄ Sn	C ₃₈ H ₂₉ F ₄ N ₂ O _{3.5} Sn
Formula weight	821.34	713.74	764.32
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	12.178(3)	6.8849(17)	9.0937(18)
<i>b</i> (Å)	12.210(3)	9.689(2)	12.383(3)
<i>c</i> (Å)	13.528(3)	20.087(5)	15.671(3)
α (°)	85.800(3)	92.768(3)	88.772(3)
β (°)	71.632(4)	96.930(3)	77.385(3)
γ (°)	75.559(3)	106.223(3)	88.877(3)
<i>V</i> (Å ³)	1848.8(8)	1272.5(5)	1721.5(6)
<i>Z</i>	2	2	2
<i>D</i> _{calc} (Mg m ⁻³)	1.475	1.863	1.475
<i>F</i> (000)	828	688	770
μ (mm ⁻¹)	0.794	2.044	0.804
Crystal size (mm)	0.44 × 0.23 × 0.12	0.56 × 0.49 × 0.42	0.47 × 0.45 × 0.26
θ Range	1.72–25.01	2.05–25.00	2.10–25.01
Index ranges	–7 ≤ <i>h</i> ≤ 14 –12 ≤ <i>k</i> ≤ 14 –15 ≤ <i>l</i> ≤ 16	–8 ≤ <i>h</i> ≤ 5 –11 ≤ <i>k</i> ≤ 11 –23 ≤ <i>l</i> ≤ 23	–10 ≤ <i>h</i> ≤ 10 –14 ≤ <i>k</i> ≤ 10 –17 ≤ <i>l</i> ≤ 18
Reflections collected	9768	6618	9079
Unique reflections (<i>R</i> _{int})	6443 (0.0235)	4400 (0.0179)	5996 (0.0283)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max/min transmission	0.9108, 0.7215	0.4806, 0.3940	0.8181, 0.7036
Data, restraints, parameters	6443, 0, 478	4400, 0, 307	5996, 327, 458
GOF	0.988	0.998	1.003
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0398, <i>wR</i> ₂ = 0.0866	<i>R</i> ₁ = 0.0361, <i>wR</i> ₂ = 0.0962	<i>R</i> ₁ = 0.0465, <i>wR</i> ₂ = 0.1106
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0662, <i>wR</i> ₂ = 0.1032	<i>R</i> ₁ = 0.0457, <i>wR</i> ₂ = 0.1031	<i>R</i> ₁ = 0.0674, <i>wR</i> ₂ = 0.1255

correction was applied to the data. The structure was solved by direct methods using SHELXLS-97 and refined against *F*² by full matrix least squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Tables 4 and 5.

4. Supplementary material

CCDC 609762, 609764, 609765, 609766, 609763 and 609767 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **6** and **7**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgement

We thank the National Nature Science Foundation of China (20271025) for financial support.

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